Nucleophilic Trifluoromethylation of Unactivated Arenes

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1. NMR Spectra for Photolysis of Complex 2

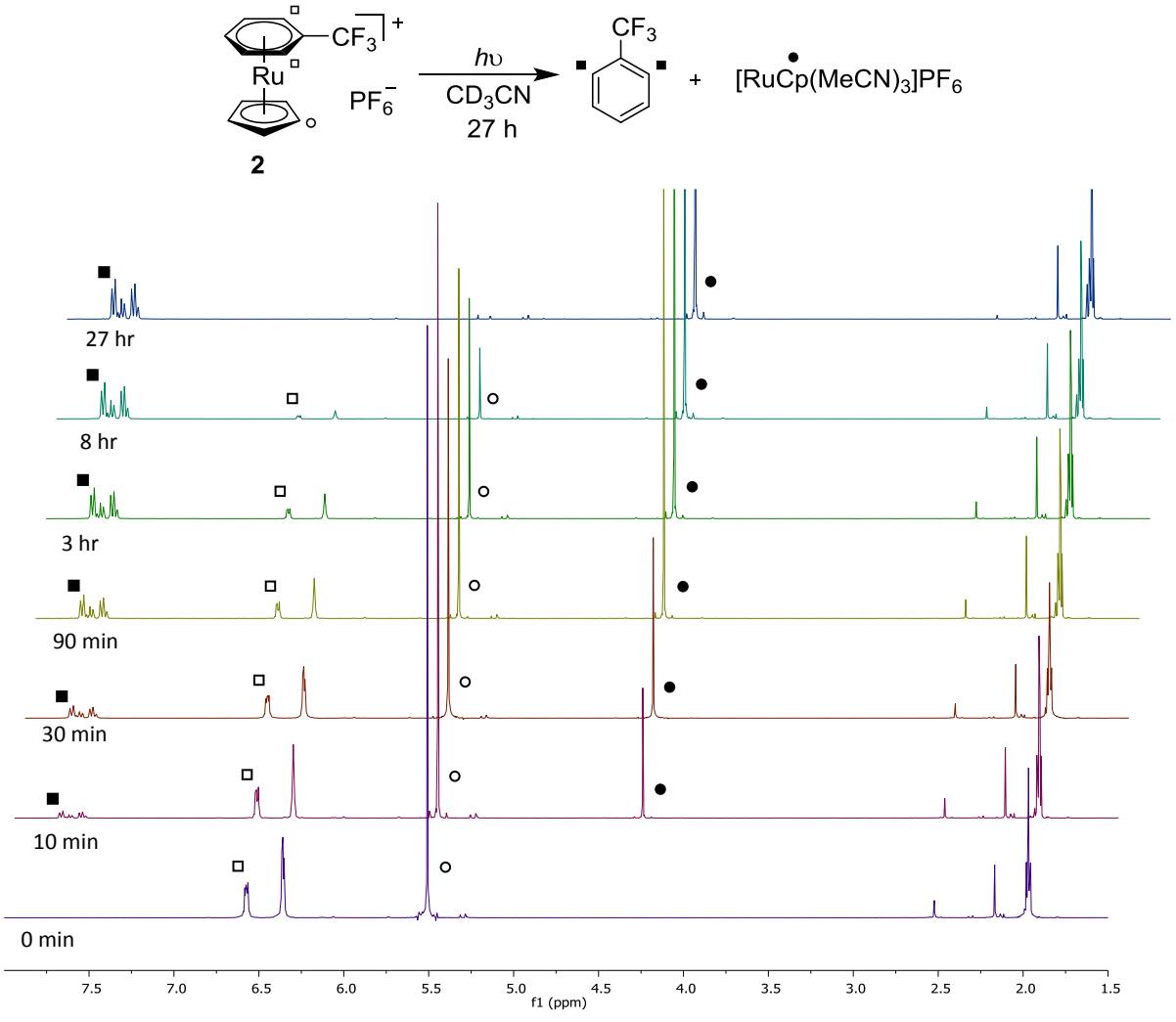
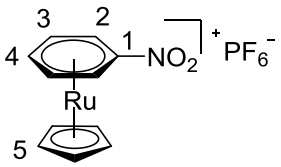


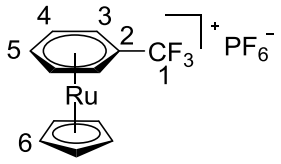
Figure S1. Stacked ^{1}H-NMR spectra (CD_3CN, 298 K, 400 MHz) for the photolysis of complex **2**.

2. Experimental Detail and Product Characterisation



[Ru(η^6-nitrobenzene)(η^5-cyclopentadienyl)]PF$_6$ ***(1)***

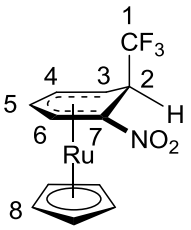
To a solution of nitrobenzene (63 mg, 53 µL, 0.507 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (9 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF$_6$ (200 mg, 0.461 mmol). The resulting solution was heated to reflux for 16 hours under an inert atmosphere, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et$_2$O. The green solid was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (187 mg, 93%); **δ$_H$** (acetone-D$_6$) 7.46 (2H, dt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 2.0 Hz, H^2), 6.79 (2H, tt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 2.0 Hz, H^3), 6.70 (1H, tt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 2.0 Hz, H^4) 5.78 (5H, s, H^5); **δ$_C$** (acetone-D$_6$) 111.4 (1C, s, C^1), 88.5 (1C, s, C^4), 86.5 (2C, s, C^3), 83.7 (5C, s, C^5), 82.9 (2C, s, C^2); **δ$_P$** (acetone-D$_6$) -144.3 (sept., $J_{P\text{-}F}$ 707 Hz); *m/z* (HRMS$^+$) 283.9788 [M-PF$_6$]$^+$ (C$_{11}$H$_{10}$NO$_2$^{96}Ru requires 283.9787); Anal. Found (Expected): C 30.47 (30.43); H 2.34 (2.32); N 3.37 (3.23).



[Ru(η^6-α,α,α-trifluorotoluene)(η^5-cyclopentadienyl)]PF$_6$ ***(2)***

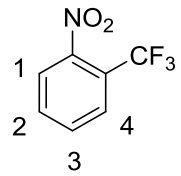
[Ru(η^6-nitrobenzene)(η^5-cyclopentadiene)]PF$_6$ (100 mg, 0.230 mmol) was dissolved in anhydrous DMF (5 mL). Oven dried potassium fluoride (15 mg, 0.253 mmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (36 mg, 37.4 µL, 0.253 mmol, 1.1 equiv) were added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column chromatography (silica, acetonitrile : 5% MeOH) gave the *title compound* as a brown solid (33 mg, 31%); **δ$_H$** (acetone-D$_6$) 6.86 – 6.82 (2H, m, H^3), 6.64 – 6.61 (3H, m, H$^{4 \text{ and } 5}$), 5.70 (5H, s, H^6); **δ$_C$** (acetone-D$_6$) 123.2 (1C, q, $^1J_{C\text{-}F}$ 274 Hz, C^1), 91.8 (1C, q, $^2J_{C\text{-}F}$ 38 Hz, C^2),

87.8 (1C, s, C^5), 86.2 (2C, s, C^4), 83.6 (2C, q, $^3J_{C\text{-}F}$ 3 Hz, C^3), 82.6 (5C, s, C^6); $\boldsymbol{\delta_F}$ (acetone-D_6) -62.33 (3F, s, F^{arene}), -72.6 (6F, d, $^1J_{F\text{-}P}$ 707 Hz, $F^{counterion}$); *m/z* (HRMS$^+$) 306.9812 [M-PF_6]$^+$ ($C_{12}H_{10}F_3{}^{96}Ru$ requires 306.9811) R_f= 0.17 (silica, acetonitrile : 5% MeOH); Anal. Found (Expected): C 31.69 (31.52); H 2.21 (2.20); N 0.26 (0.00).



[Ru(η^5-1-nitro-2-trifluoromethylcyclohexadienyl)(η^5-cyclopentadiene)] ***(3)***

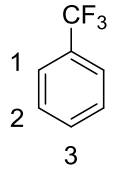
[Ru(η^6-nitrobenzene)(η^5-cyclopentadiene)]PF_6 (100 mg, 0.230 mmol) was dissolved in anhydrous DMF (5 mL). Oven dried potassium fluoride (15 mg, 0.253 mmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (36 mg, 37.4 µL, 0.253 mmol, 1.1 equiv) was added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column chromatography (silica, pet. ether : 20% EtOAc) gave the *title compound* as a yellow oil (27 mg, 32%); $\boldsymbol{\delta_H}$ (acetone-D_6) 6.19 (1H, td, $^3J_{H\text{-}H}$ 5.5 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^5), 6.09 (1H, ddd, $^3J_{H\text{-}H}$ 5.5 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, $^4J_{H\text{-}H}$ 0.5 Hz, H^6), 5.09 (1H, t, $^3J_{H\text{-}H}$ 5.5 Hz, H^4), 4.96 (5H, s, H^8), 4.48 (1H, qdd, $^3J_{H\text{-}F}$ 8.0 Hz, $^3J_{H\text{-}H}$ 6.5 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^2), 3.76 (1H, dt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^3); $\boldsymbol{\delta_C}$ (acetone-D_6) 124.1 (1C, q, $^1J_{C\text{-}F}$ 287 Hz, C^1), 81.0 (1C, s, C^4), 80.6 (1C, s, C^5), 79.4 (5C, s, C^8), 75.1 (1C, s, C^6), 62.0 (1C, m, C^7), 43.4 (1C, q, $^2J_{C\text{-}F}$ 29 Hz, C^2), 28.3 (1C, q, $^1J_{C\text{-}F}$ 2 Hz, C^3); $\boldsymbol{\delta_F}$ (acetone-D_6) -76.4 (3F, d, $^3J_{F\text{-}H}$ 8.0 Hz); *m/z* (HRMS$^+$) 353.9818 [M+H]$^+$ ($C_{12}H_{11}F_3NO_2{}^{96}Ru$ requires 353.9818), 306.9811 [M-NO_2]$^+$ ($C_{12}H_{10}F_3{}^{96}Ru$ requires 306.9811), R_f= 0.28 (silica, pet. ether : 20% EtOAc).



2-Trifluoromethyl-nitrobenzene

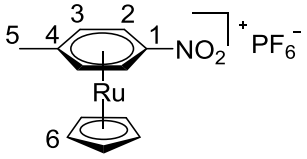
To an oven dried Schlenk tube, [Ru(η^5-1-nitro-2-trifluoromethylcyclohexadienyl)(η^5-cyclopentadiene)] (20 mg, 55.8 µmol) was added and dissolved in anhydrous deuterated

acetonitrile (1 mL). To this, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (15 mg, 66.9 µmol, 1.2 equiv) was added and the mixture was stirred at room temperature for 24 hours. ^{1}H- and ^{19}F-NMR showed confirmation of quantitative conversion to free arene using an external standard of α,α,α-trifluorotoluene (10 mg, *quantitative*); **δ_H** (acetonitile-D_3) 8.00 (1H, m), 7.96 (1H, m), 7.89 (2H, m); **δ_F** (acetonitrile-D_3) -60.2 (3F, m).



α,α,α-Trifluorotoluene

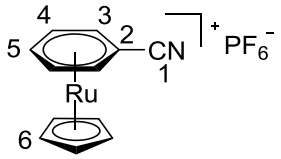
To a quartz NMR tube, [Ru(η^6-α,α,α-trifluorotoluene)(η^5-cyclopentadienyl)]PF_6 (20 mg, 43.7 µmol) was added and dissolved in anhydrous deuterated acetonitrile (0.8 mL). The mixture was irradiated under UV lamp (365 mn, 36 W) for 27 hours to give the *title compound* in a quantitative conversion (see NMR spectrum S1). **δ_H** (acetonitile-D_3) 7.73 (2H, m, H^1), 7.68 (1H, t, $^{3}J_{H\text{-}H}$ 7.5, H^3) 7.60 (2H, t, $^{3}J_{H\text{-}H}$ 7.5, H^2); **δ_F** (acetonitrile-D_3) -63.2 (3F, m).



[Ru(η^6-4-nitrotoluene)(η^5-cyclopentadienyl)]PF_6

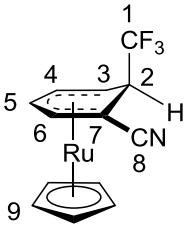
To a solution of 4-nitrotoluene (19 mg, 0.138 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (4 mL) at 80 °C was added [Ru$(NCMe)_3$Cp]PF_6 (50 mg, 0.115 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (56 mg, 91%). **δ_H** (acetone-D_6) 7.39 (2H, d, $^{3}J_{H\text{-}H}$ 6.5 Hz, H^2), 6.77 (2H, d, $^{3}J_{H\text{-}H}$ 6.5 Hz, H^3), 5.73 (5H, s, H^6), 2.54 (3H, s, H^5); **δ_C** (acetone-D_6) 110.5 (1C, s, C^1), 105.8 (1C, s, C^4), 88.6 (2C, s, C^3), 87.6 (1C, s, C^5), 83.3 (5C, s, C^6), 72.9 (1C, s, C^2); **δ_P** (acetone-D_6) -144.3 (sept, $^{1}J_{P\text{-}F}$ 713 Hz); **δ_F** (acetone-D_6) -72.2 (d, $^{1}J_{F\text{-}P}$ 713 Hz); *m/z*

(HRMS$^+$) 297.9946 [M – PF_6]$^+$ ($C_{12}H_{12}NO_2{}^{96}Ru$ requires 297.9944); Anal. Found (Expected): C 31.38 (32.15); H 2.71 (2.70); N 3.30 (3.12).



[Ru(η^6-benzonitrile)(η^5-cyclopentadienyl)]PF_6

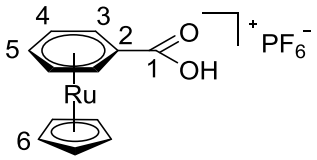
To a solution of benzonitrile (26 mg, 26 µL, 0.253 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (6 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF_6 (100 mg, 0.230 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (85 mg, 89%). $\boldsymbol{\delta_H}$ (acetone-D_6) 6.89 (2H, dt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^3), 6.65 (2H, tt, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^4), 6.61 (1H, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^5), 5.77 (5H, s, H^6); $\boldsymbol{\delta_C}$ (acetone-D_6) 115.3 (1C, s, C^1), 88.6 (2C, s, C^3), 87.6 (1C, s, C^5), 86.7 (2C, s, C^4), 83.3 (5C, s, C^6), 72.9 (1C, s, C^2); $\boldsymbol{\delta_P}$ (acetone-D_6) -144.3 (sept, $^1J_{P\text{-}F}$ 713 Hz); $\boldsymbol{\delta_F}$ (acetone-D_6) -72.2 (d, $^1J_{F\text{-}P}$ 713 Hz); *m/z* (HRMS$^+$) 263.9888 [M – PF_6]$^+$ ($C_{12}H_{10}N^{96}Ru$ requires 263.9889); Anal. Found (Expected): C 34.85 (34.79); H 2.56 (2.43); N 3.43 (3.38).



*[Ru(η^5-1-cyano-2-trifluoromethylcyclohexadienyl)(η^5-cyclopentadiene)]**(4b)***

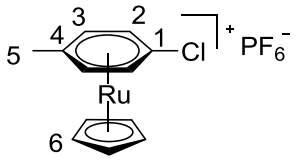
[Ru(η^6-benzonitrile)(η^5-cyclopentadiene)]PF_6 (20 mg, 48.3 µmol) was dissolved in anhydrous DMF (3 mL). Oven dried potassium fluoride (4 mg, 53.1 µmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (8 mg, 9 µL, 53.1 µmol, 1.1 equiv) was added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column

chromatography (silica, pet. ether : 20% EtOAc) gave the *title compound* as a brown oil (6 mg, 36%). $\boldsymbol{\delta_H}$ (acetone-D_6) 6.13 (1H, td, $^3J_{H\text{-}H}$ 5.5 Hz, $^4J_{H\text{-}H}$ 1.0 Hz, H^5), 5.25 (1H, d, $^3J_{H\text{-}H}$ 5.5 Hz, H^6), 5.05 (5H, s, H^9), 4.94 (1H, t, $^3J_{H\text{-}H}$ 5.5 Hz, H^4), 3.48 (1H, qdd, $^3J_{H\text{-}F}$ 7.5 Hz, $^3J_{H\text{-}H}$ 5.5 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^2), 3.33 (1H, t, $^3J_{H\text{-}H}$ 5.5 Hz, H^3); $\boldsymbol{\delta_C}$ (acetone-D_6) 124.1 (1C, q, $^1J_{C\text{-}F}$ 286 Hz, C^1), 123.2 (1C, m, C^8), 81.9 (1C, s, C^5), 80.4 (1C, s, C^4), 79.0 (5C, s, C^9), 78.8 (1C, s, C^6), 44.2 (1C, q, $^2J_{C\text{-}F}$ 29 Hz, C^2), 24.1 (1C, q, $^1J_{C\text{-}F}$ 2 Hz, C^3), 7.07 (1C, s, C^7); $\boldsymbol{\delta_F}$ (acetone-D_6) -78.7 (3F, d, $^3J_{F\text{-}H}$ 8.0 Hz); *m/z* (HRMS$^+$) 333.9921 $[M+H]^+$ ($C_{13}H_{11}F_3N^{96}Ru$ requires 333.9920), R_f= 0.24 (silica, pet. ether : 20% EtOAc).



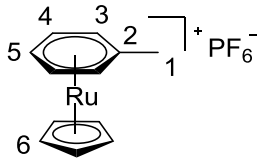
[Ru(η^6-carboxybenzene)(η^5-cyclopentadienyl)]PF_6

To a solution of benzoic acid (17 mg, 0.138 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (6 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF_6 (50 mg, 0.115 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (47 mg, 94%). $\boldsymbol{\delta_H}$ (acetone-D_6) 6.88 (2H, d, $^3J_{H\text{-}H}$ 6.0 Hz, H^3), 6.56 (2H, t, $^3J_{H\text{-}H}$ 6.0 Hz, H^4), 6.53 (1H, $^3J_{H\text{-}H}$ 6.0 Hz, H^5), 5.60 (5H, s, H^6); $\boldsymbol{\delta_C}$ (acetone-D_6) 165.3 (1C, s, C^1), 88.5 (1C, s, C^2), 87.3 (1C, s, C^5), 86.7 (2C, s, C^4), 86.5 (2C, s, C^3), 81.8 (5C, s, C^6); $\boldsymbol{\delta_P}$ (acetone-D_6) -144.3 (sept, $^1J_{P\text{-}F}$ 713 Hz); $\boldsymbol{\delta_F}$ (acetone-D_6) -72.2 (d, $^1J_{F\text{-}P}$ 713 Hz); *m/z* (HRMS$^+$) 282.9834 $[M - PF_6]^+$ ($C_{12}H_{11}O_2{}^{96}Ru$ requires 282.9835); Anal. Found (Expected) for $C_{12}H_{11}F_6O_2PRu.(MeCN)_{0.15}$: C 33.95 (33.62); H 2.70 (2.63); N 0.27 (0.48).



[Ru(η^6-4-chlorotoluene)(η^5-cyclopentadienyl)]PF_6

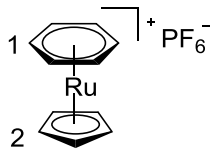
To a solution of 4-chlorotoluene (48 mg, 45 µL, 0.380 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (8 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF_6 (150 mg, 0.345 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (147 mg, 97%). $\boldsymbol{\delta_H}$ (acetone-D$_6$) 6.81 – 6.74 (2H, m, H^2), 6.55 – 6.48 (2H, m, H^3), 5.63 (5H, s, H^6), 2.42 (3H, s, H^5); $\boldsymbol{\delta_C}$ (acetone-D$_6$) 104.7 (1C, s, C^1), 102.6 (1C, s, C^4), 87.2 (2C, s, C$^{2/3}$), 86.9 (2C, s, C$^{2/3}$), 83.0 (5C, s, C^6), 20.0 (1C, s, C^5); $\boldsymbol{\delta_P}$ (acetone-D$_6$) -144.3 (sept, $^1J_{P\text{-}F}$ 713 Hz); $\boldsymbol{\delta_F}$ (acetone-D$_6$) -72.2 (d, $^1J_{F\text{-}P}$ 713 Hz); *m/z* (HRMS$^+$) 286.9705 [M – PF_6]$^+$ ($C_{12}H_{12}{}^{35}Cl^{96}Ru$ requires 286.9704).



[Ru(η^6-toluene)(η^5-cyclopentadienyl)]PF_6

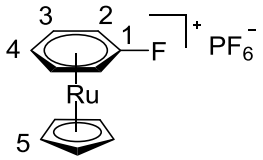
To a solution of toluene (24 mg, 27 µL, 0.253 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (5 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF_6 (100 mg, 0.230 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a light brown solid (87 mg, 94%). $\boldsymbol{\delta_H}$ (acetone-D$_6$) 6.35-6.38 (2H, m, H^3), 6.27-6.32 (2H, m, H^4), 6.22-6.26 (1H, m, H^5) 5.51 (5H, s, H^6), 2.39 (3H, s, H^1); $\boldsymbol{\delta_C}$ (acetone-D$_6$) 102.6 (1C, s, C^2), 87.2 (2C, s, C^3), 85.4 (2C, s, C^4), 84.7 (1C, s, C^5), 80.5 (5C, s, C^6), 19.7 (1C, s, C^1); $\boldsymbol{\delta_P}$ (acetone-D$_6$) -144.3 (sept, $^1J_{P\text{-}F}$ 713 Hz); $\boldsymbol{\delta_F}$ (acetone-D$_6$) -72.2 (d, $^1J_{F\text{-}P}$ 713

Hz); *m/z* (ESI$^+$) 253.0098 $[M\text{-}PF_6]^+$ ($C_{12}H_{13}{}^{96}Ru$ requires 253.0093). Anal. Found (Expected): C 35.67 (35.74); H 3.36 (3.25); N 0.32 (0.00).



[Ru(η^6-benzene)(η^5-cyclopentadienyl)]PF_6

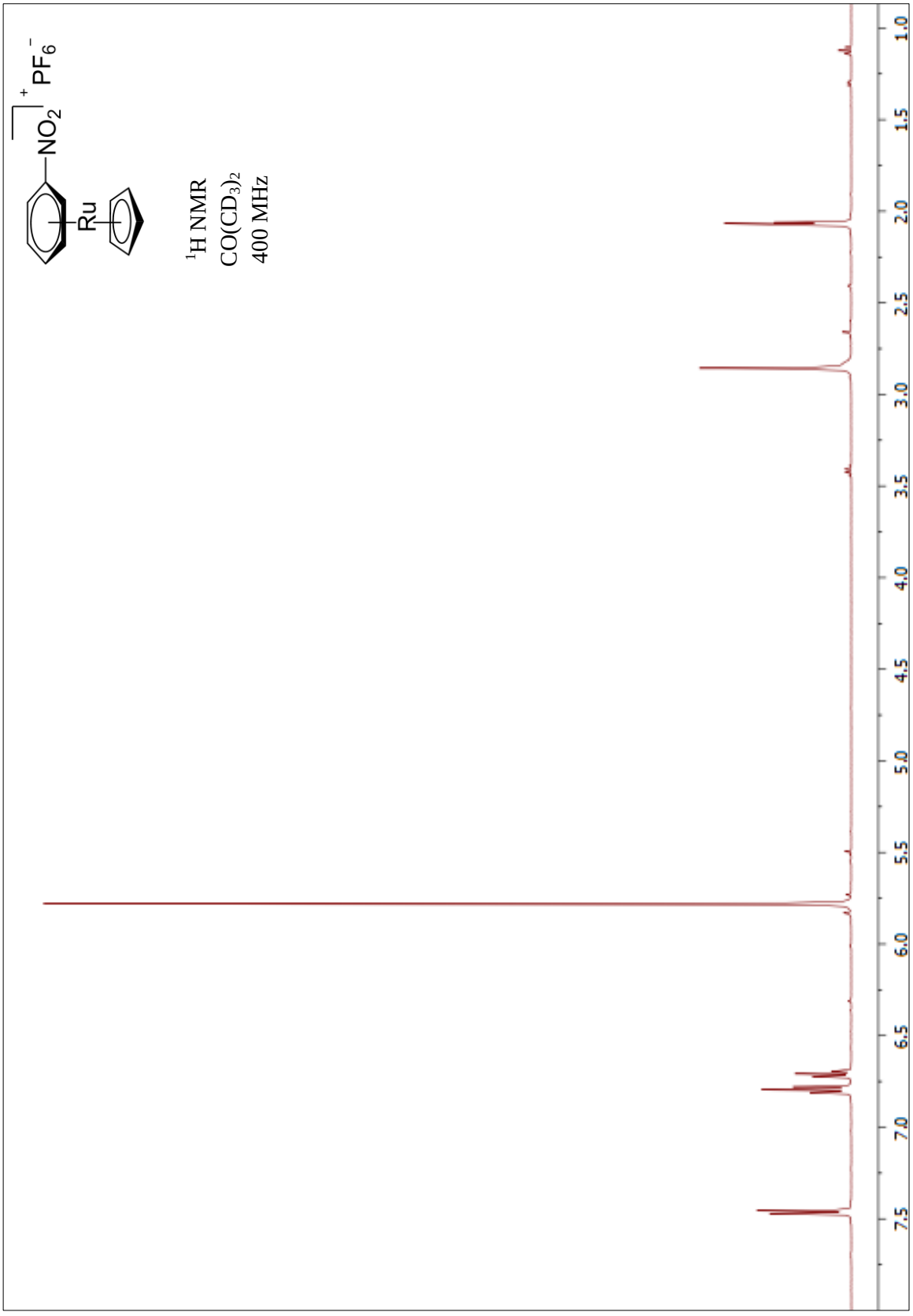
The reaction is a modification of the existing literature procedure.[1] A 100 mL oven dried round-bottom flask equipped with a stir-bar was charged with finely ground potassium carbonate (0.83 g, 6.00 mmol, 6.0 equiv) and the flask flame-dried under vacuum. After cooling to room temperature, the flask was further charged with $[(C_6H_6)RuCl_2]_2$ (0.50 g, 1.00 mmol) and a reflux condenser added. Ethanol (30 mL) was then added, followed by freshly cracked cyclopentadiene (1.5 mL, 18.0 mmol, 18 equiv). The resulting heterogeneous brown mixture was then warmed to 85 °C with rapid stirring. After approximately 16 h, the reaction mixture was cooled to room temperature and filtered through a plug of Celite, and the Celite rinsed with a further 25 mL of ethanol. The dark yellow filtrate was concentrated to 20 mL, then an aqueous solution of NH_4PF_6 (0.68 g, 4.20 mmol, 4.2 equiv, in 10 mL of H_2O) was added, resulting in the immediate formation of a tan precipitate. The remaining ethanol was removed under reduced pressure and the resulting suspension cooled for several hours. The mixture was then filtered and the tan solid dried under vacuum. The crude product was subsequently dissolved in a minimum of acetonitrile and diethyl ether added dropwise until precipitate formation was no longer observed. This mixture was cooled for several hours before being filtered to give the *title compound* as a light brown solid 0.718 g (92%). The product is spectroscopically identical to the known $[(\eta^6\text{-}C_6H_6)Ru(C_5H_5)]PF_6$[2] and is pure by ^{1}H NMR spectroscopy to the limits of detection. $\boldsymbol{\delta_H}$ (acetone-D_6) 6.36 (6H, s, H^1), 5.56 (5H, s, H^2).

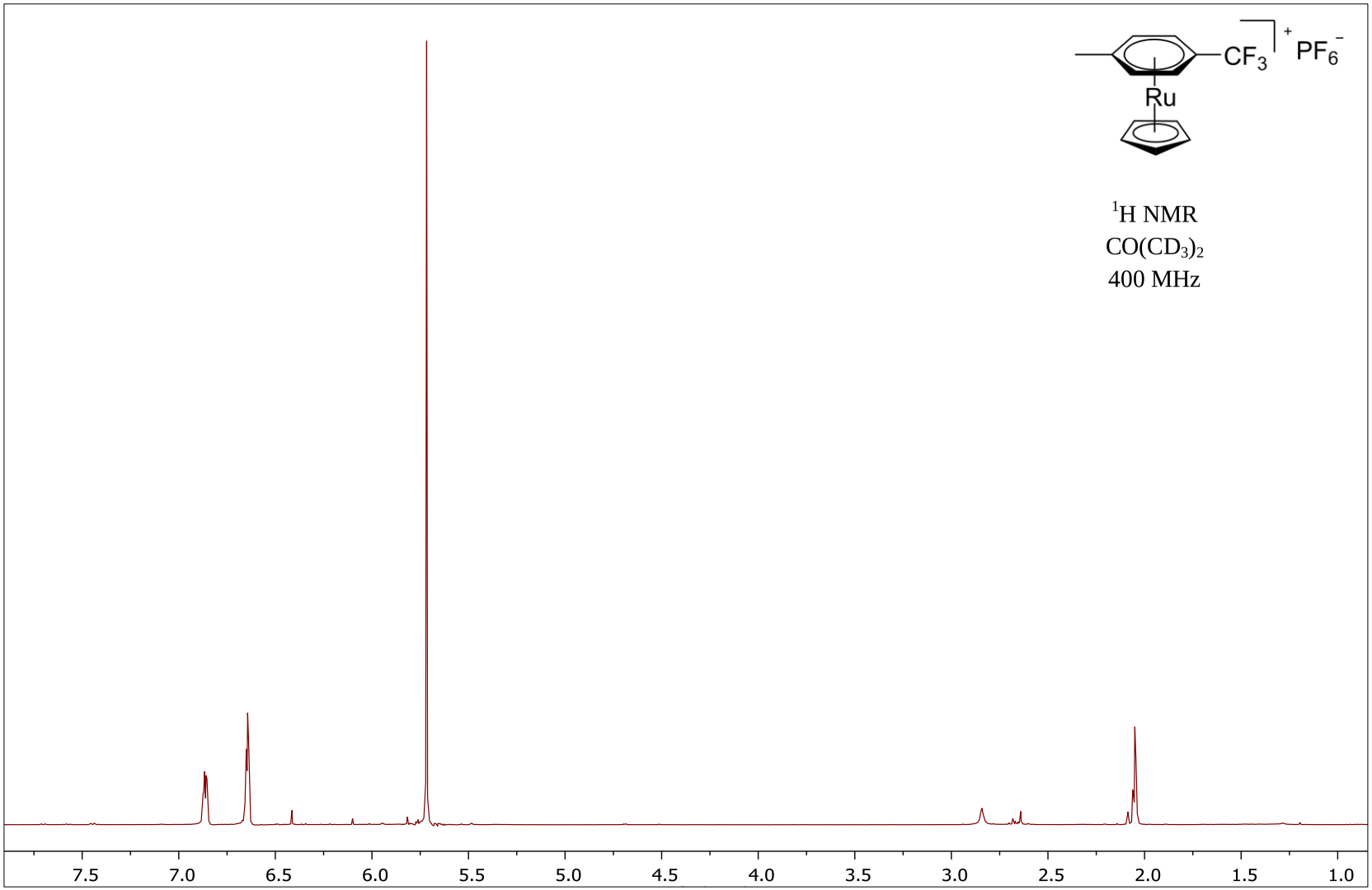


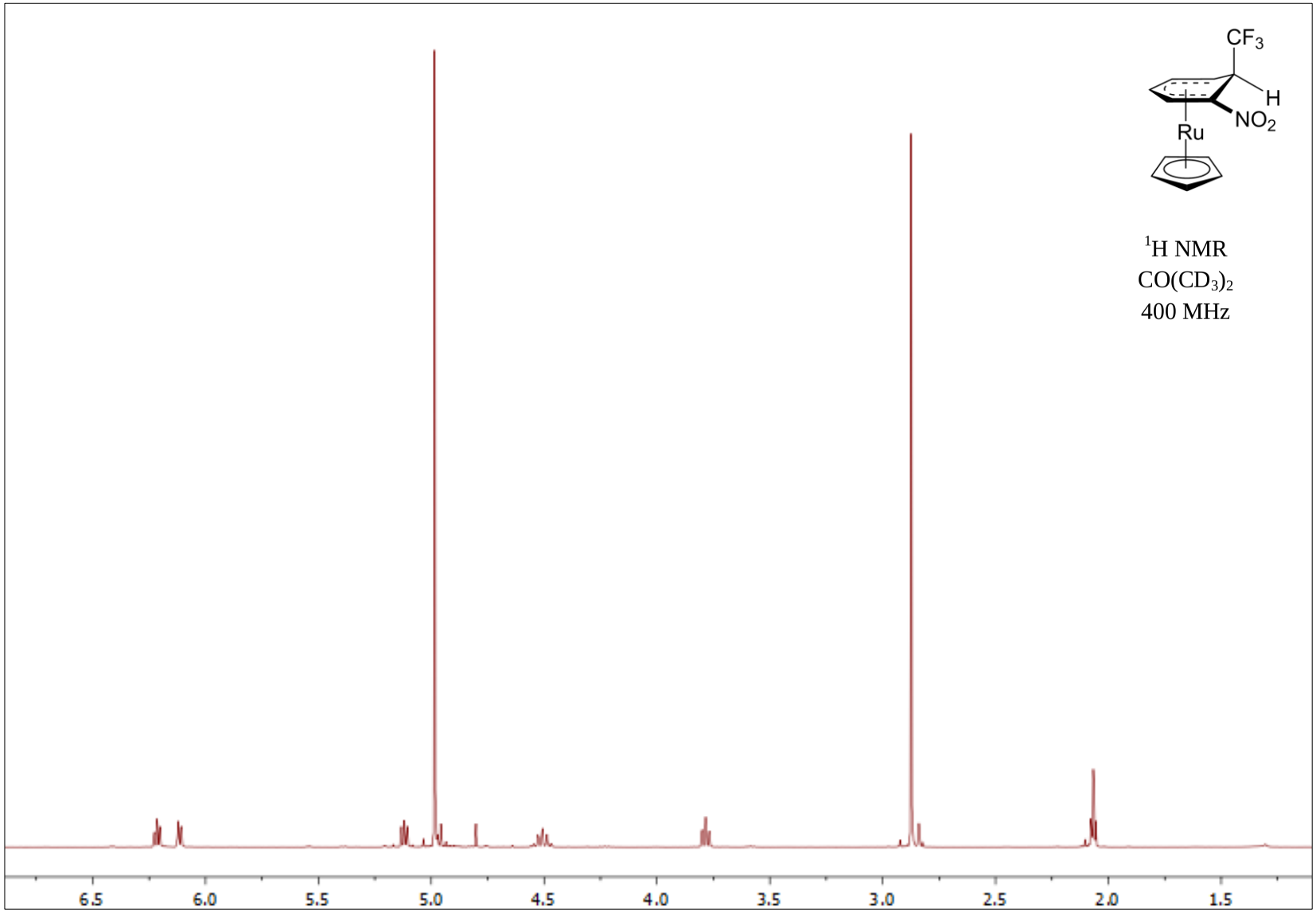
[Ru(η^6-fluorobenzene)(η^5-cyclopentadienyl)]PF_6

To a solution of fluorobenzene (48 mg, 47 µL, 0.507 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (9 mL) at 80 °C was added $[Ru(NCMe)_3Cp]PF_6$ (200 mg, 0.461 mmol). The resulting solution was heated to reflux for 16 hours under an inert atmosphere, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et_2O. The brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the *title compound* as a brown solid (153 mg, 82%); $\boldsymbol{\delta_H}$ (acetone-D_6) 6.82 (2H, dd, $^3J_{H\text{-}H}$ 6.0 Hz, $^3J_{H\text{-}F}$ 4.5 Hz, H^2), 6.47 (2H, td, $^3J_{H\text{-}H}$ 6.0 Hz, $^4J_{H\text{-}F}$ 4.0 Hz, H^3), 6.27 (1H, td, $^3J_{H\text{-}H}$ 6.0 Hz, $^5J_{H\text{-}F}$ 3.5 Hz, H^4) 5.65 (5H, s, H^5); $\boldsymbol{\delta_C}$ (acetone-D_6) 136.9 (1C, d, $^1J_{C\text{-}F}$ 276 Hz, C^1), 85.2 (1C, s, C^4), 84.9 (2C, d, $^3J_{C\text{-}F}$ 6 Hz, C^3), 81.6 (5C, s, C^5), 77.4 (2C, d, $^2J_{C\text{-}F}$ 21 Hz, C^2); $\boldsymbol{\delta_F}$ (acetone-D_6) -72.6 (6F, d, $^1J_{F\text{-}P}$ 707 Hz, $F^{counterion}$), -137.5 (1F, m, F^{arene}); $\boldsymbol{\delta_P}$ (acetone-D_6) -144.3 (sept., $J_{P\text{-}F}$ 707 Hz); *m/z* (HRMS$^+$) 256.9836 $[M\text{-}PF_6]^+$ ($C_{11}H_{10}F^{96}Ru$ requires 256.9842). Anal. Found (Expected): C 32.56 (32.44); H 2.52 (2.48); N 0.25 (0.00).

3. NMR spectra of Products




CF3
+
PF6
-
Ru
1H NMR
CO(CD3)2
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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H
NO2
Ru
1H NMR
CO(CD3)2
400 MHz
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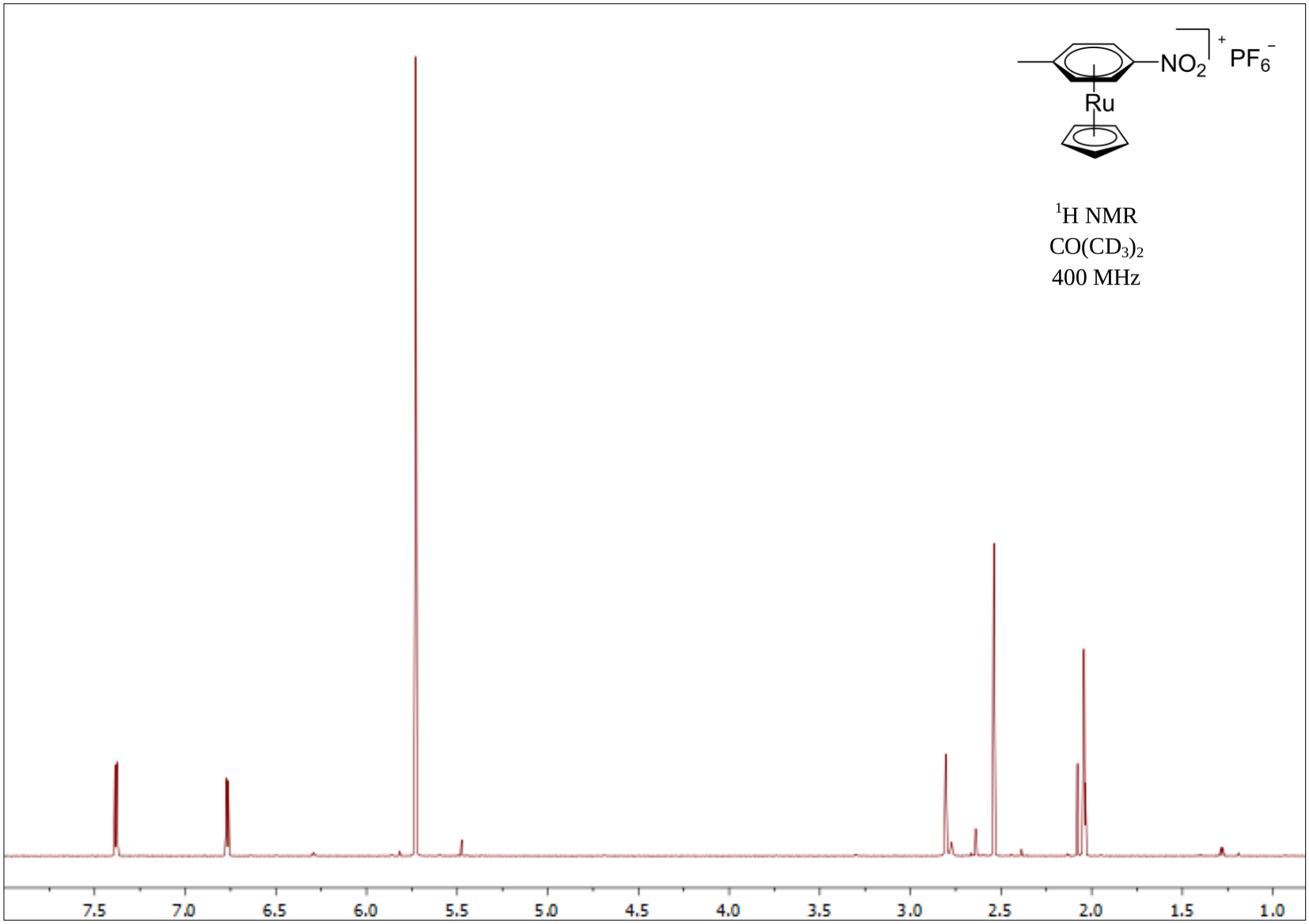
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5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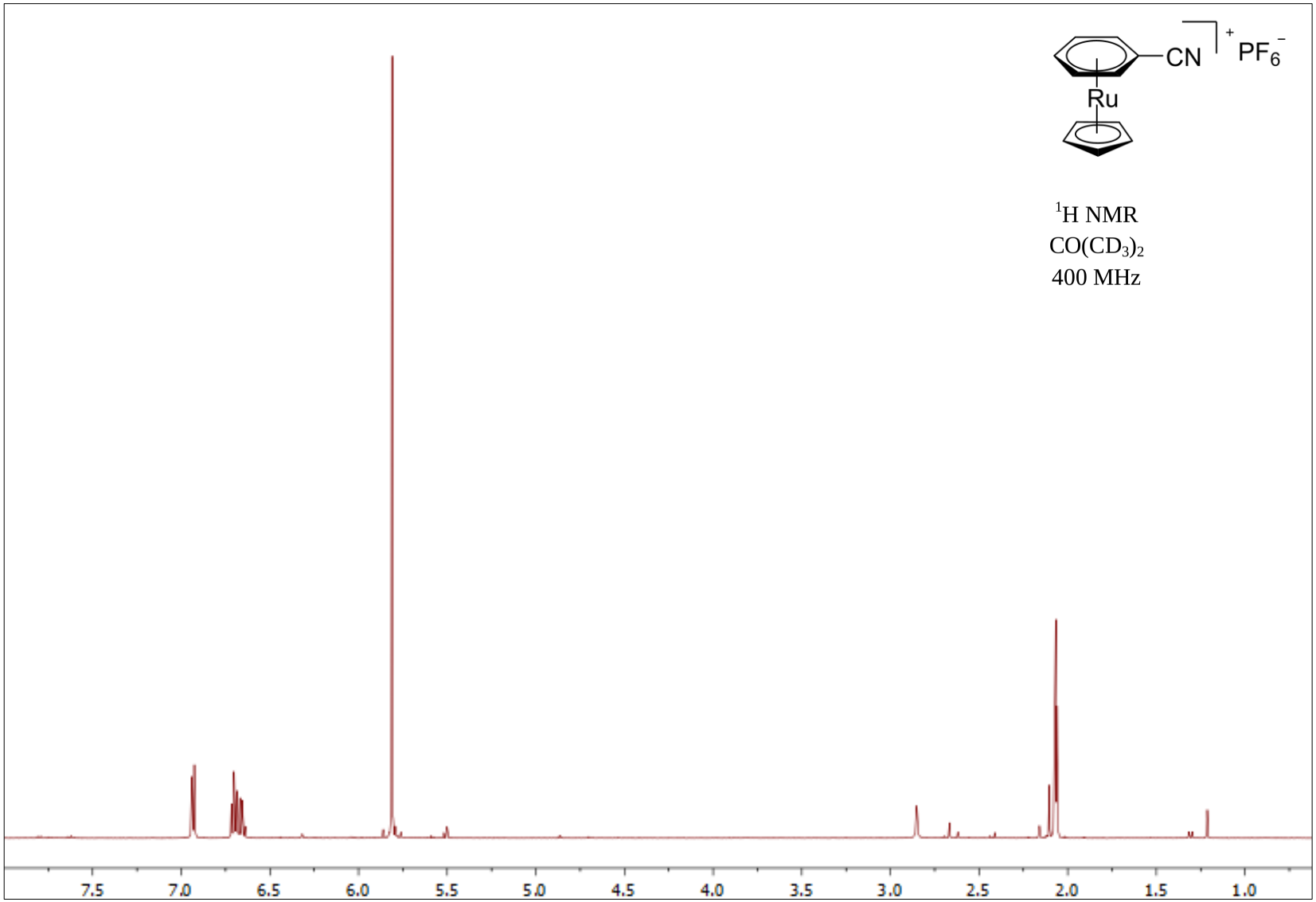
+
PF6
-
Ru
1H NMR
CO(CD3)2
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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PF6
-
Ru
1H NMR
CO(CD3)2
400 MHz
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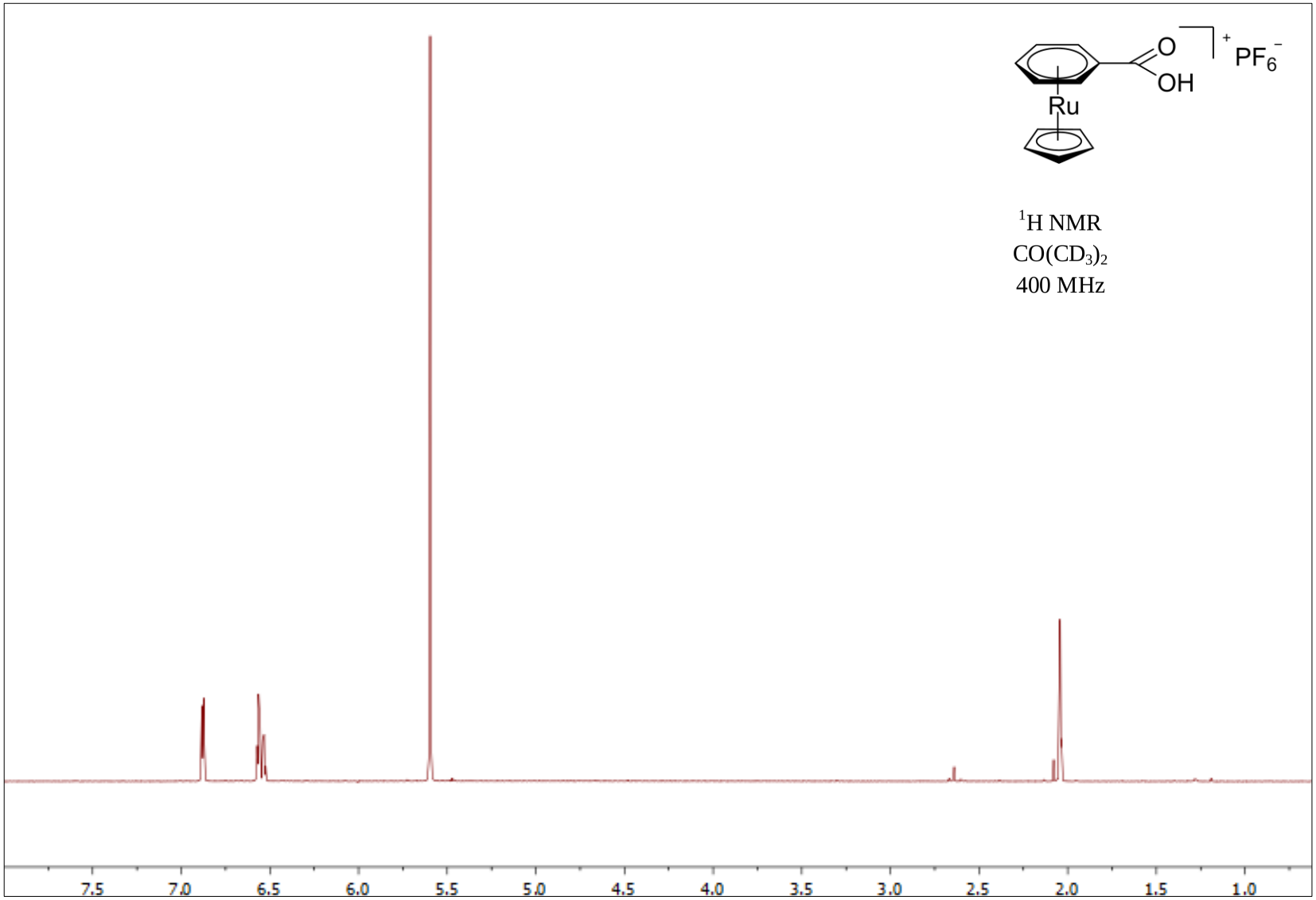
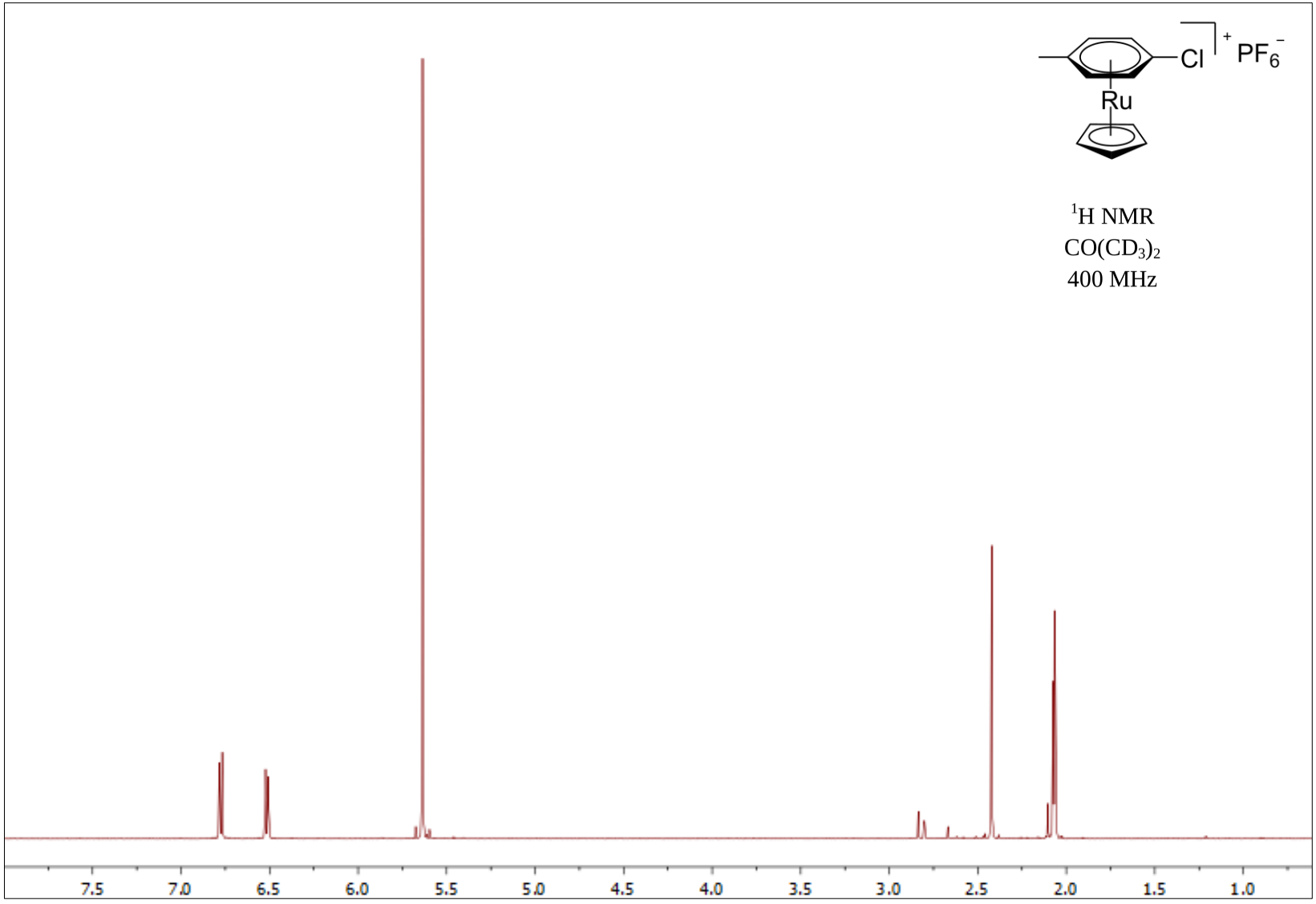
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


O
OH
Ru
+
PF6 -
1H NMR
CO(CD3)2
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


Cl
+
PF6
-
Ru
1H NMR
CO(CD3)2
400 MHz
7.5
7.0
6.5
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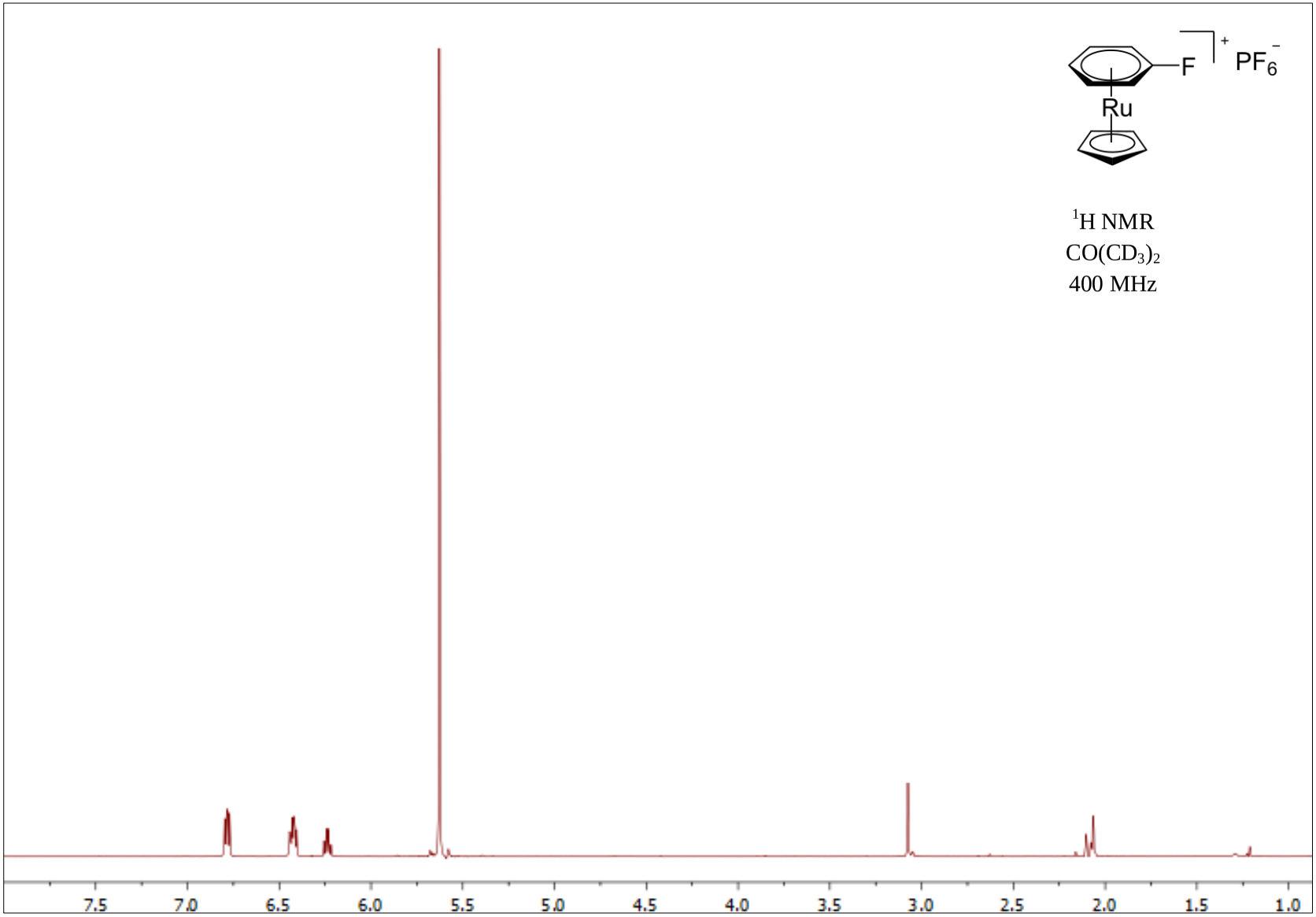
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


F
+
PF6
-
Ru
1H NMR
CO(CD3)2
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

1. Crystal and Structural Refinement Data for Complex 1

The X-ray single crystal data have been collected using λMoKα radiation (λ =0.71073Å) on an Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2)K. The structure was solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [3] and SHELXTL [4] software. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions and refined in riding mode. Crystal data and parameters of refinement are listed in Table S1. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1546706.

2. **Table S1**. Crystal data and structure refinement for **1**

Empirical formula	$C_{11}H_{10}NO_2Ru$ x PF_6
Formula weight	434.24
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.17160(16)
b/Å	12.4722(2)
c/Å	13.2874(3)
α/°	90.00
β/°	91.5709(18)
γ/°	90.00
Volume/$Å^3$	1353.72(5)
Z	4
$\rho_{calc}g/cm^3$	2.131
μ/mm^{-1}	1.352
F(000)	848.0
Crystal size/mm^3	0.38 × 0.31 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.48 to 60
Index ranges	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$

Reflections collected	20965
Independent reflections	3953 [R_{int} = 0.0336, R_{sigma} = 0.0243]
Data/restraints/parameters	3953/0/199
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0975
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1033
Largest diff. peak/hole / e $Å^{-3}$	1.29/-0.95

References

1 B. M. Trost and C. M. Older, *Organometallics*, 2002, 21, 2544–2546.

2 T. P. Gill and K. R. Mann, *Organometallics*, 1982, 1, 485–488

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. *Appl. Cryst.* (2009), 42, 339-341.

4 G.M. Sheldrick, *Acta Cryst.* (2008), A64, 112-122.